



Effect of Electron Beam Irradiation on the Tensile Properties of Carbon Nanotube Sheets and Yarns

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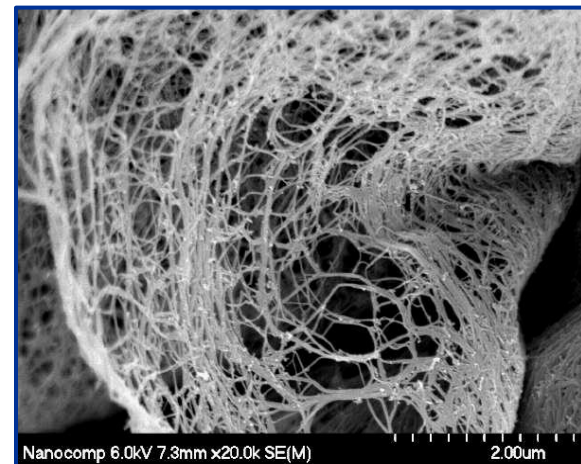


Presentation outline

- Background and Motivation
- Experimental
- Results and Discussion
- Conclusions

Background and Motivation

- Lightweight materials and structures
 - Reduced vehicle mass
 - Incorporation of nanostructured reinforcement could decrease aircraft and spacecraft weight by one-third
- Strength of carbon nanotubes (CNTs)
 - 1 TPa E' and 100 GPa tensile strength (SWNTs via arc discharge)
- Properties much lower in commonly used nanomanufacturing methods
- Weakness attributed to entanglements, slippage of CNTs, van der Waals forces



SEM image of Nanocomp CNT sheet

Goal is to investigate various routes to introduce covalent crosslinks in CNTs via e-beam irradiation for increased tensile strength

Crosslinking of CNTs

- **Common irradiation methods¹⁻⁴**
 - Microwave irradiation
 - Electron beam energy
- Electron beam irradiation usually carried out using TEM
- Covalent crosslinking in CNTs is believed to take place at sites where vacancy defect edges face each other
- E-beam irradiation introduced defects (loose or dangling bonds) that can lead to crosslinking

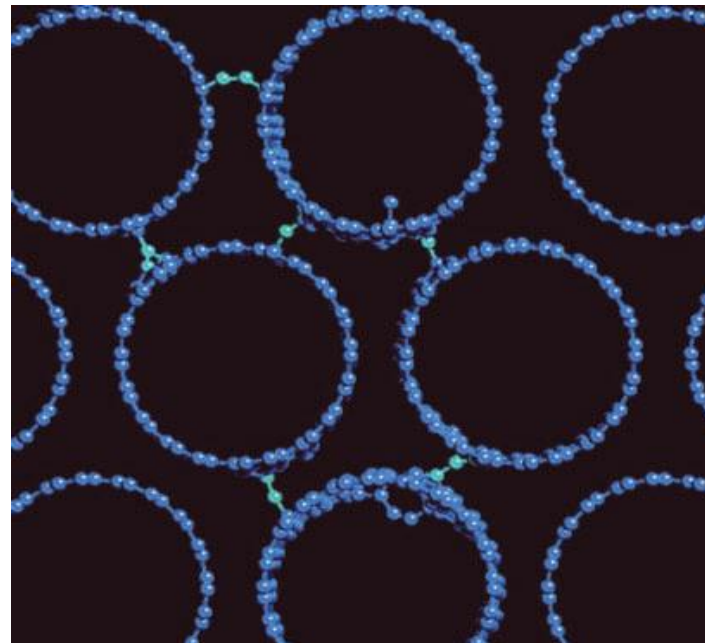


Image taken from Thess, A., *et. al*, Crystalline Ropes of Metallic Carbon Nanotubes, *Science* **273**, 483-487 (1996) and Ajayan, P. Banhart, Nanotubes Strong Bundles, *Nature Materials* **3**, 135-136 (2004)

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²Banhart, F., Irradiation of carbon nanotubes with a focused electron beam in the electron microscope, *Journal of Materials Science*, 2006, 41, 4505-4511

³Wang, S., Liang, Z., Wang, B., Zhang, C., High-strength and multifunctional macroscopic fabric of single-walled carbon nanotubes, *Advanced Materials* 2007, 19, 1257-1261

⁴Duchamp, M., Meunier, R., Smajda, R., Mionic, M., Magrez, A., Seo, J.W., Forro', L., Song, B., Toma'nek, D., Reinforcing multiwall carbon nanotubes by electron beam irradiation, *Journal of Applied Physics* 108, 2010, 084314-1—084314-6

Electron beam irradiation setup

- **Materials**

- **CNT sheets (Nanocomp)**
 - As received
 - Functionalized
 - Stretched
- **CNT yarns (General Nano and Nanocomp)**
- **Northeast Ohio (NEO) Beam Facility (Middlefield, OH)**

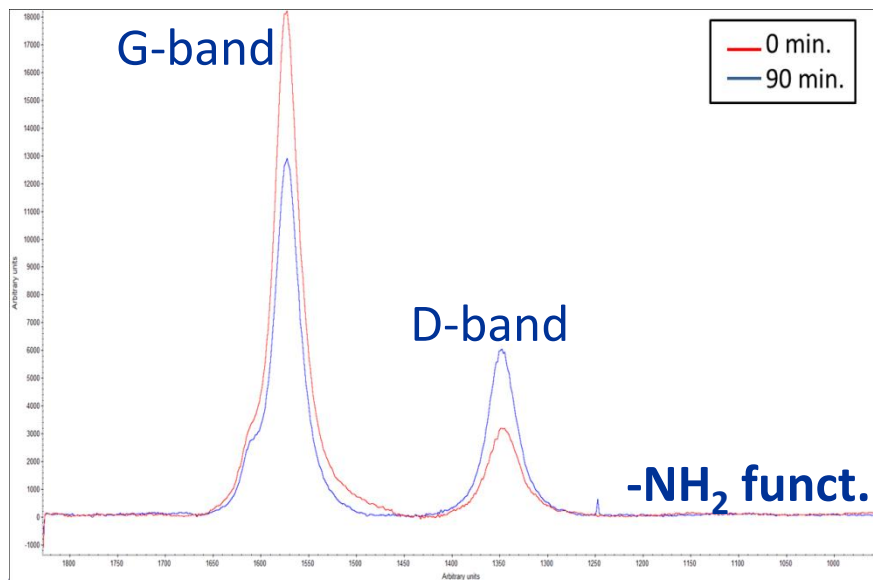
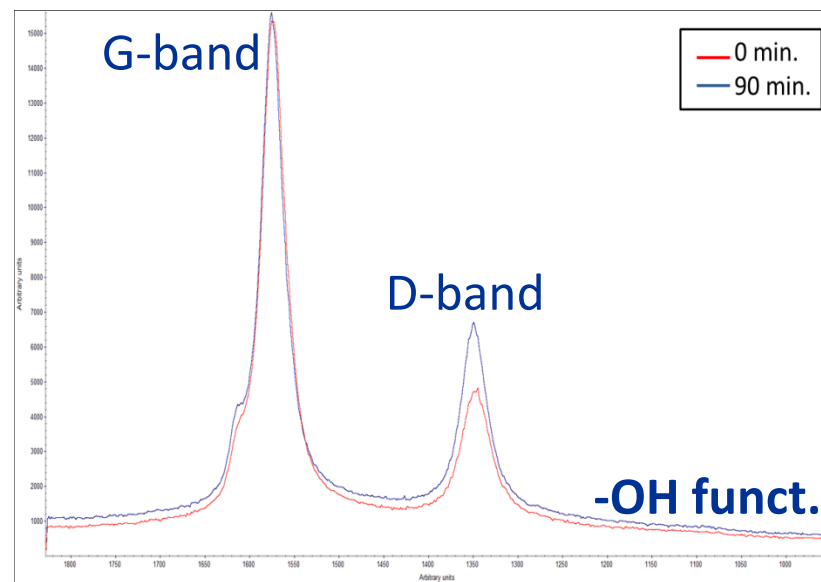
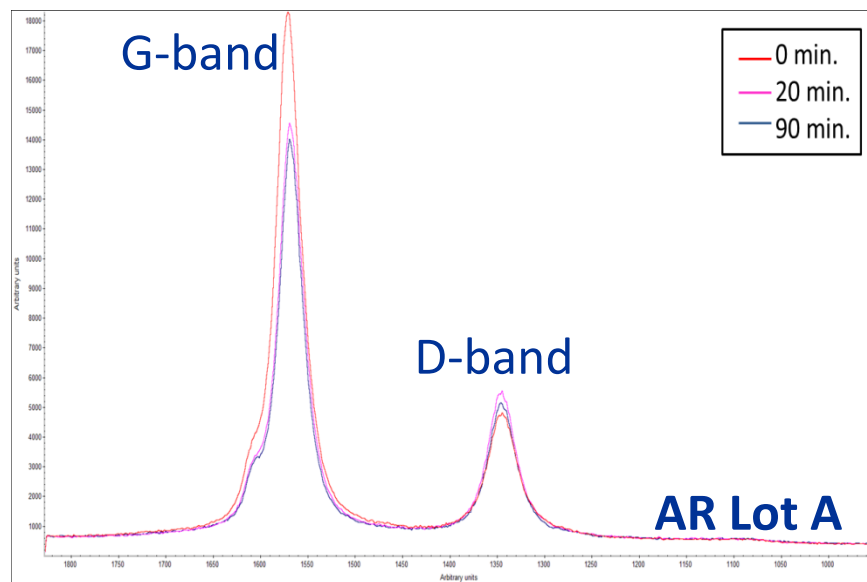
- **Energy of electrons: 2 MeV**
- **Beam current: 36 mA**
- **Irradiation time: 20-90 min.** (fluence $4.8 \times 10^{16} - 2.2 \times 10^{17} \text{ e/cm}^2$)
- **Irradiated in air**



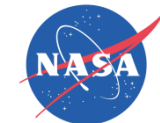
Sample stage
(water cooled)

CNT samples

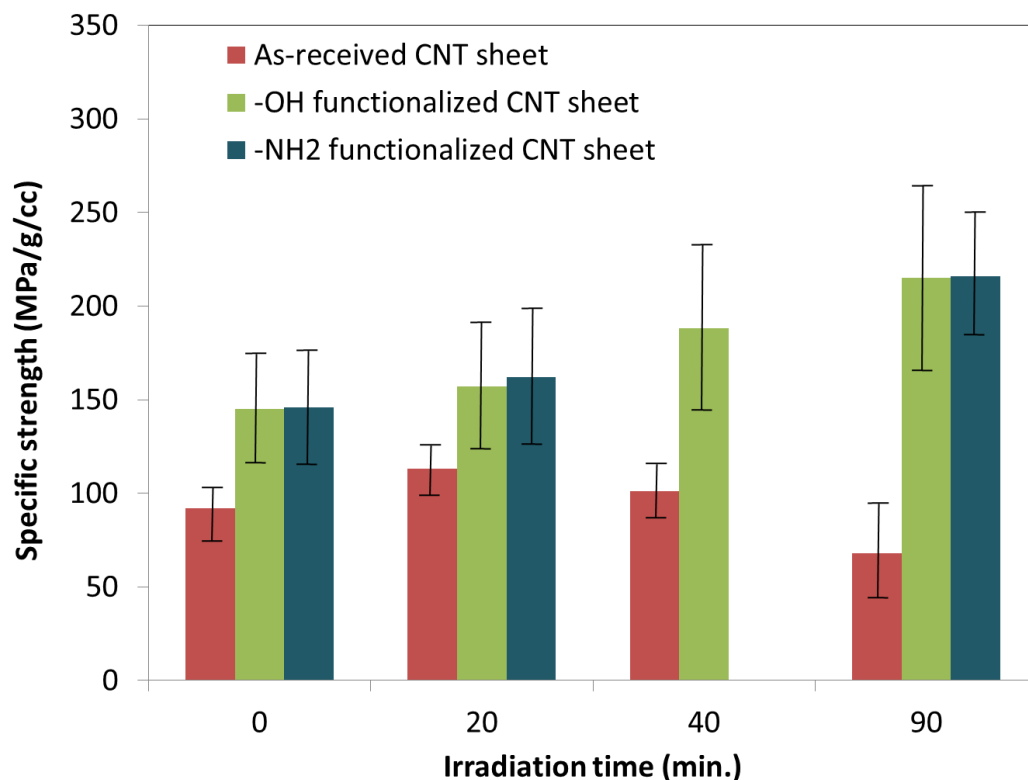
Effect of irradiation on the structure of CNT sheets



D/G ratio increased in functionalized CNT sheets as the irradiation time/dosage increased

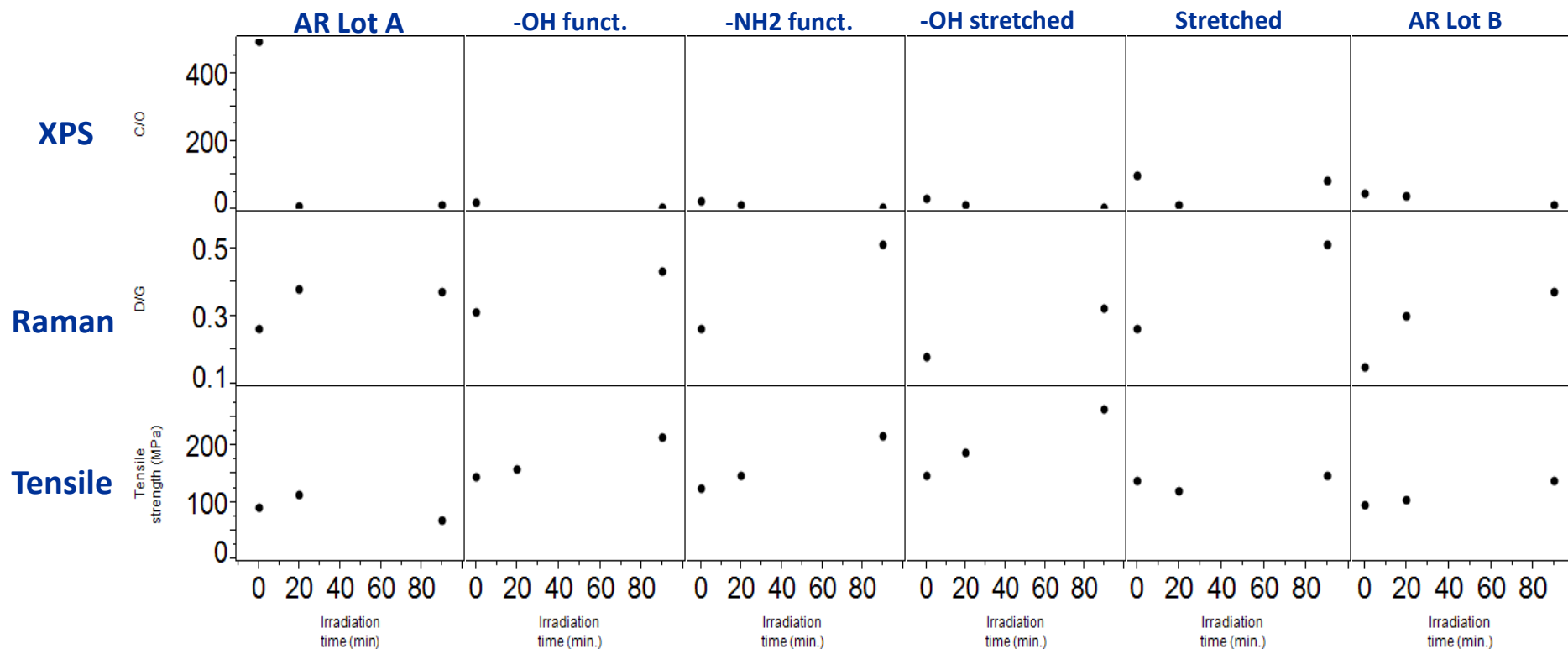


Functionalization and irradiation effects on tensile properties of CNT sheets



- As-received sheets showed minimal change in tensile strength with increasing e-beam irradiation dosage
- Higher tensile strength observed in -OH and -NH₂ functionalized irradiated sheets
- Irradiation increased tensile strength by approx. 57%
- Over 200% increase in tensile strength in functionalized, irradiated sheets compared to unfunctionalized, irradiated CNT sheets

Structure-to-property relationship comparison of irradiated CNT sheets



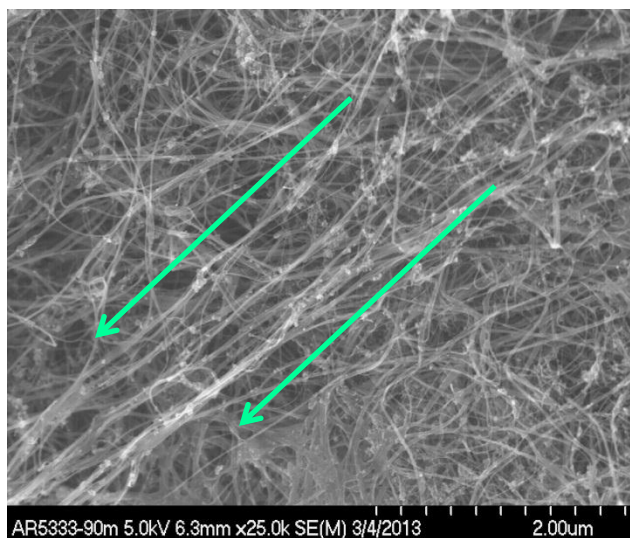
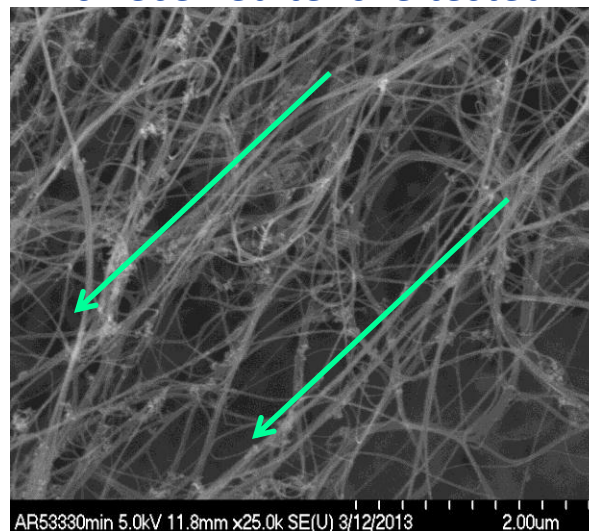
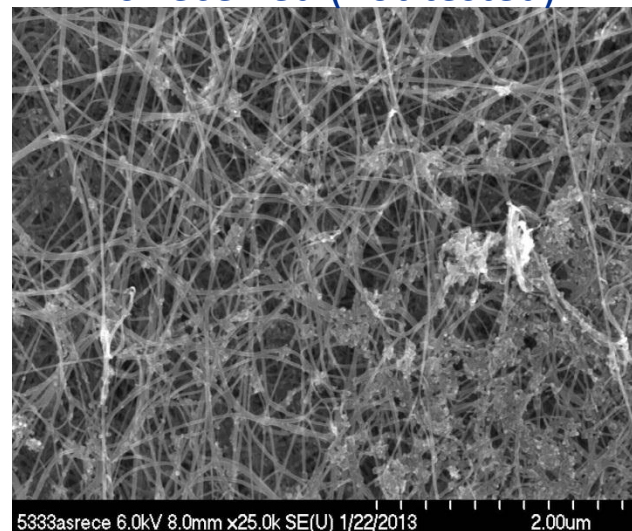
D/G ratio and tensile strength increase with increasing irradiation dosage/time
C/O ratio generally decreased with increasing irradiation dosage/time

Surface of irradiated CNT sheets (before and after tensile failure)

As-received (not tested)

As-received tensile tested

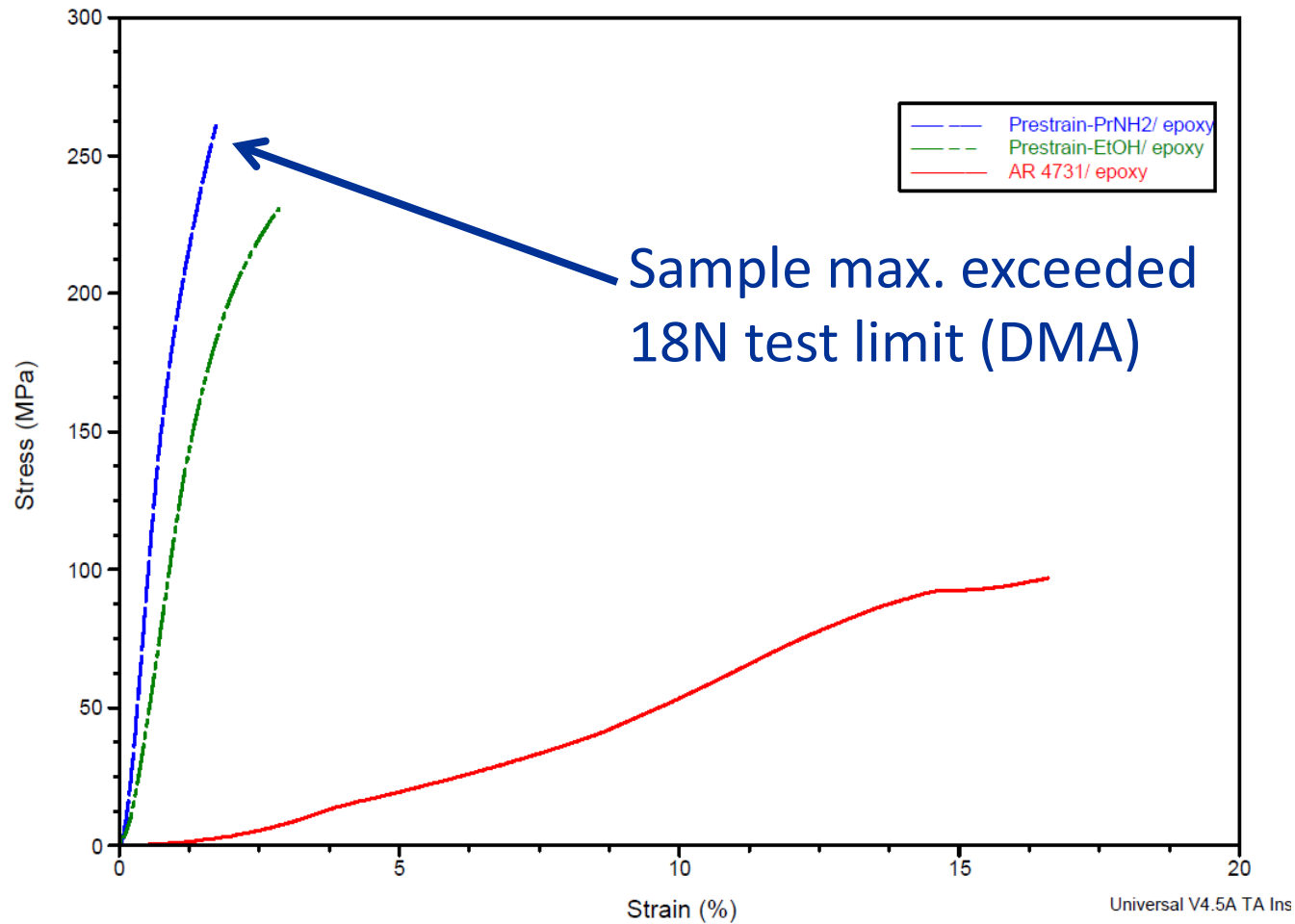
- Random orientation prior to tensile testing
- Sheets could be strained up to 25% in as-received sheets. Lower strain in irradiated sheets
- No visible changes in failure or orientation when irradiating up to 90 min



90 min irradiated tensile tested



Effect of functionalization on tensile properties of resin infused composites (DMA)

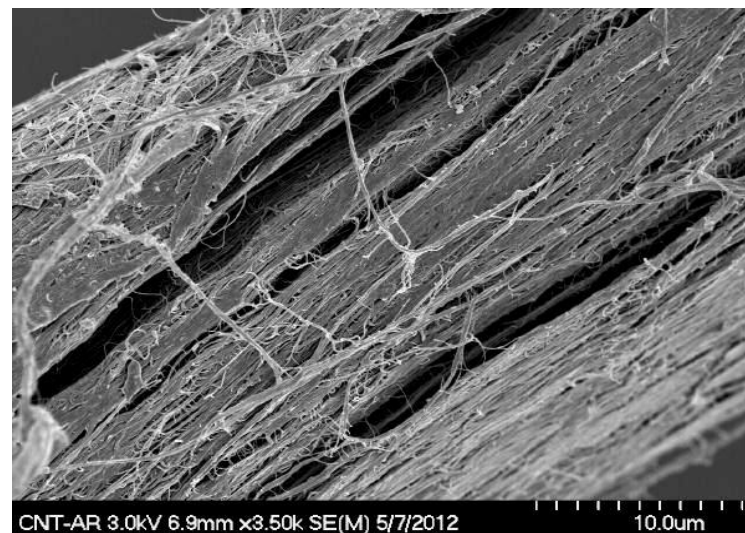
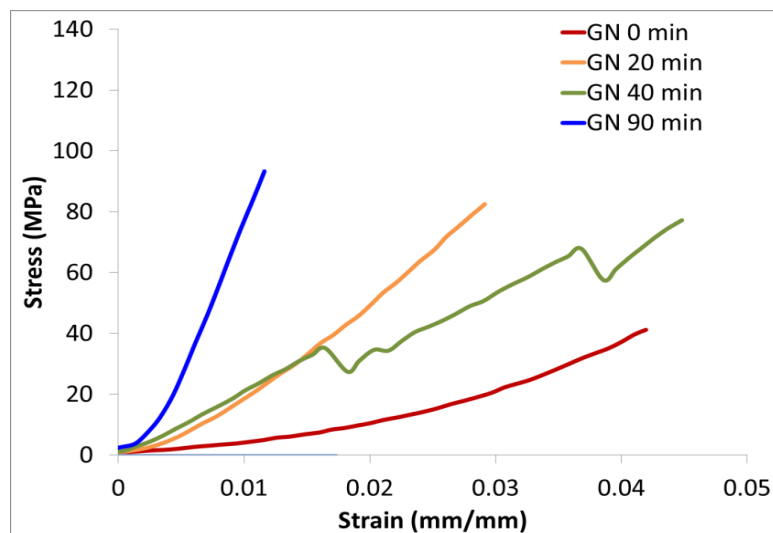
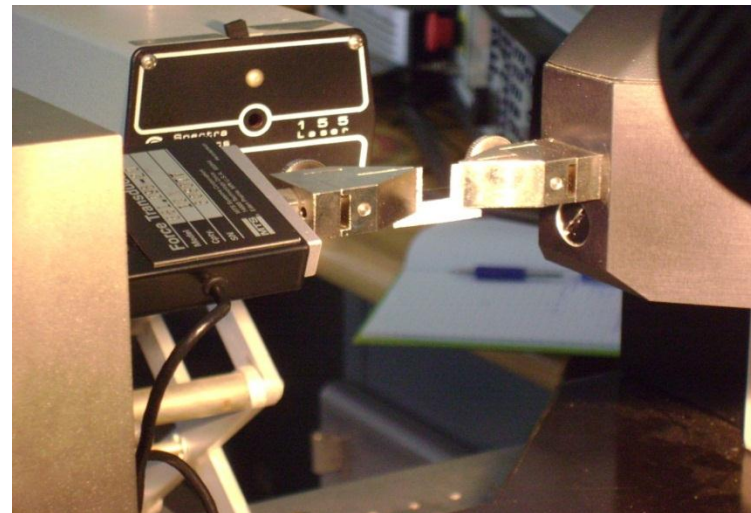


At least 160% improvement in tensile stress

Lot B CNT sheets

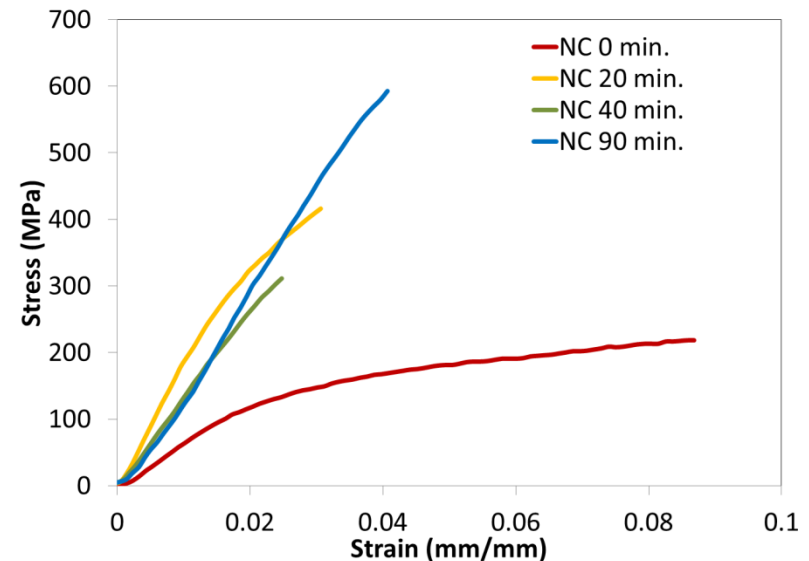
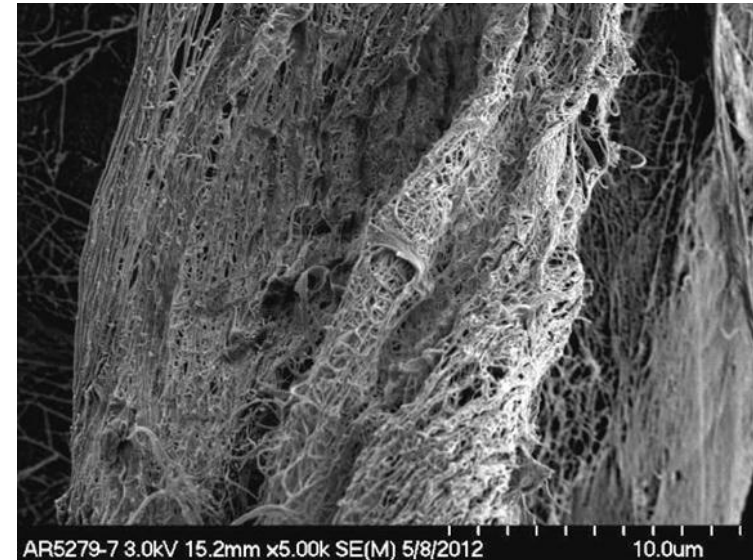
Effect of irradiation on the tensile properties of CNT yarns (General Nano)

- Mounted on paper brackets
- Tested using Tytron Microtester
- 25 N load cell
- 7-10 specimens/ sample
- Strain rate: 7.5 mm/min



Effect of irradiation on the tensile properties of CNT yarns (Nanocomp)

- Tensile stress increased with longer irradiation times
- Strain % decreased as irradiation time increased
- Tighter CNT packing in wires was believed to help with crosslinking in unfunctionalized CNT wires



Tensile properties of irradiated CNT yarns

General Nano			
	Time (min.)	Tensile stress (MPa)	Stress (N/tex)
	0	54.4 ± 20.1	0.21 ± 0.05
	20	67.9 ± 24.6	0.28 ± 0.1
	40	56.1 ± 33.9	0.20 ± 0.1
	90	90.9 ± 53.0	0.16 ± 0.08
Nanocomp			
	0	202.0 ± 28.2	0.39 ± 0.04
	20	394.5 ± 56.5	0.69 ± 0.06
	40	319.9 ± 148.1	0.6 ± 0.1
	90	587.7 ± 300.1	0.97 ± 0.1

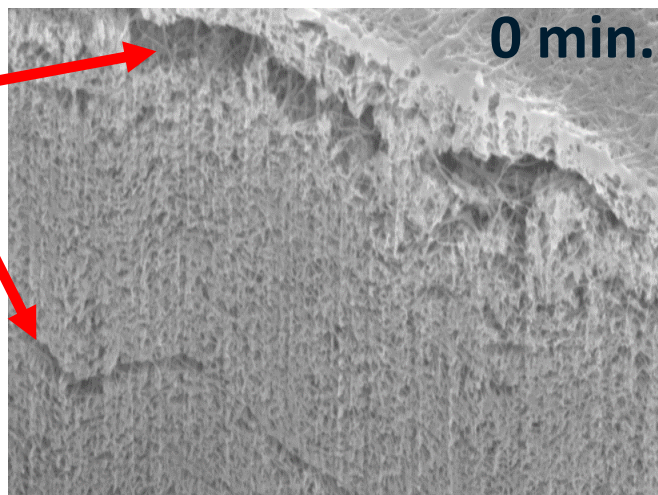


**Loose
CNT
bundles**

**Large variation in diameter
measurements**

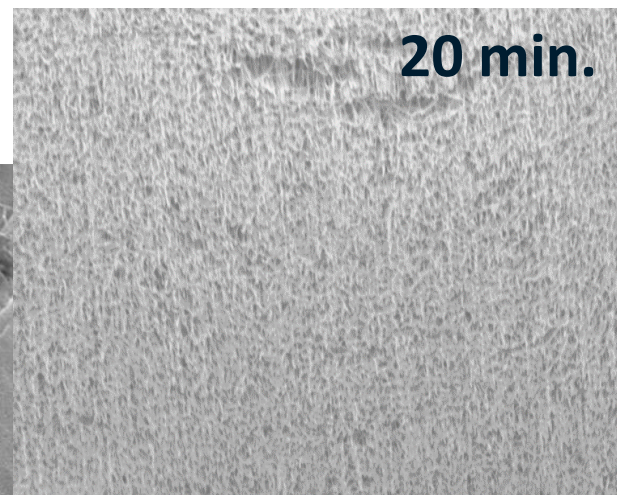
Irradiation effects on CNT yarns (Nanocomp)

Voids



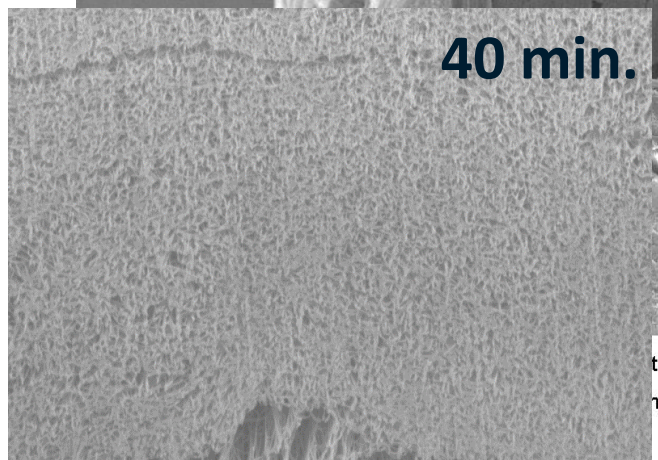
0 min.

Mag = 25.00 KX WD = 5.1 mm Signal A = InLens Tilt Corr. = On Aperture Size = 30.00 μ m FIB Probe = 30KV-50pA
1 μ m FIB Imaging = SEM EHT = 5.00 kV Tilt Angle = 54.0 $^{\circ}$ Pixel Size = 11.87 nm System Vacuum = 5.60e-006 Torr



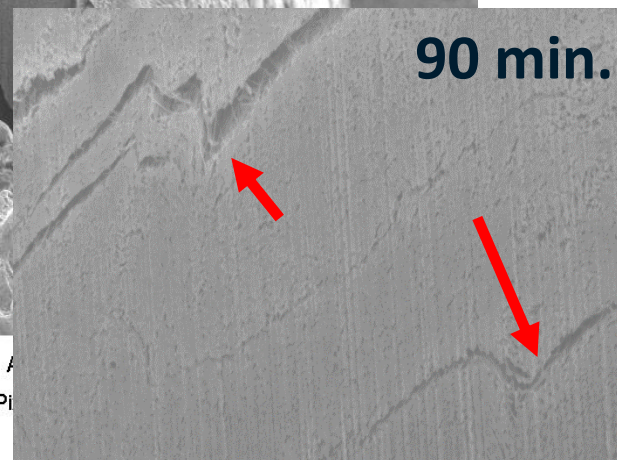
20 min.

Mag = 25.00 KX WD = 5.0 mm Signal A = InLens Tilt Corr. = On Aperture Size = 30.00 μ m FIB Probe = 30KV-50pA
1 μ m FIB Imaging = SEM EHT = 5.00 kV Tilt Angle = 54.0 $^{\circ}$ Pixel Size = 11.87 nm System Vacuum = 5.60e-006 Torr



40 min.

Mag = 25.00 KX WD = 5.1 mm Signal A = InLens Tilt Corr. = On Aperture Size = 30.00 μ m FIB Probe = 30KV-50pA
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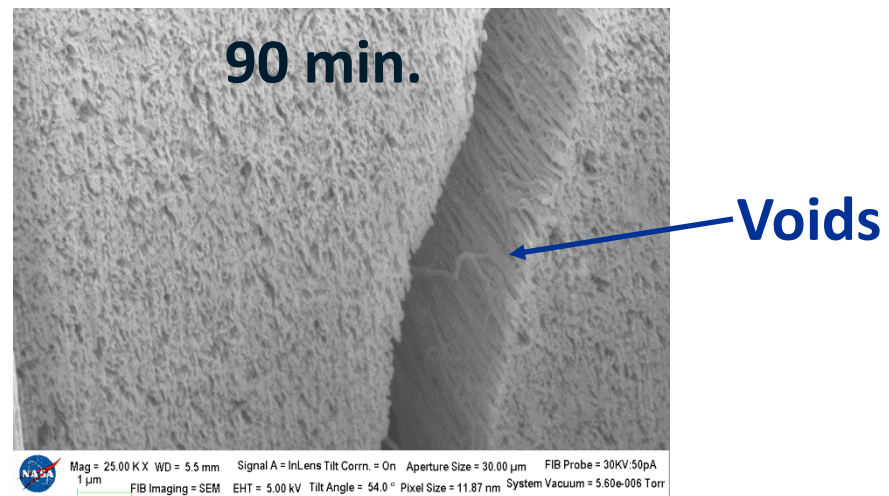
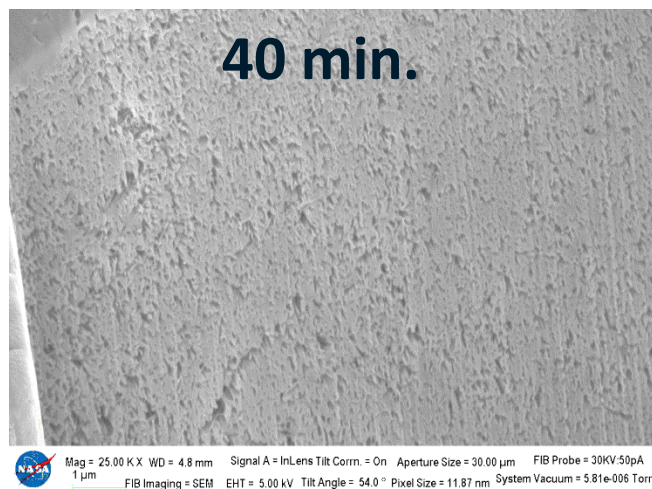
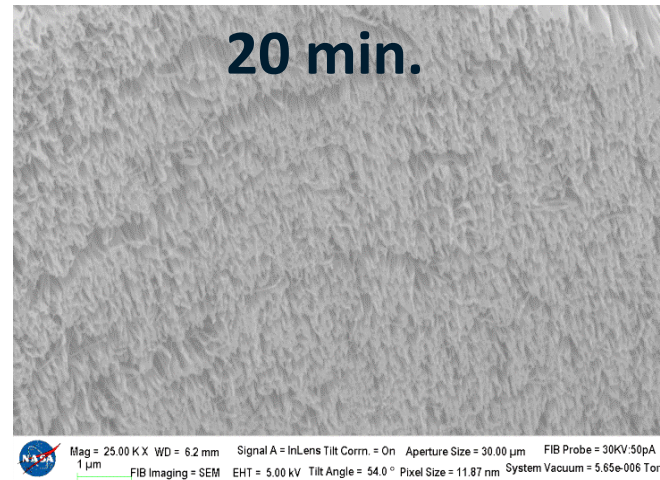
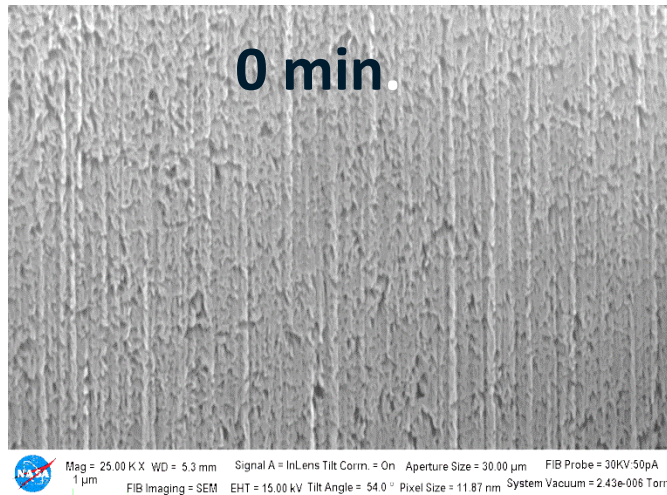


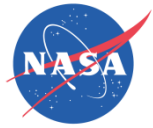
90 min.

Mag = 25.00 KX WD = 5.1 mm Signal A = InLens Tilt Corr. = On Aperture Size = 30.00 μ m FIB Probe = 30KV-50pA
1 μ m FIB Imaging = SEM EHT = 5.00 kV Tilt Angle = 54.0 $^{\circ}$ Pixel Size = 11.87 nm System Vacuum = 5.70e-006 Torr

Tighter CNT packing as irradiation time increases

Irradiation effects on CNT yarns (General Nano)





Conclusions

- Irradiating for 90 minutes led to at least a 47% increase in tensile strength for untreated CNT sheets
- Significant increase in tensile strength observed in resin infused composites containing functionalized CNT sheets compared to unfunctionalized CNT sheets
- FIB microscopy revealed CNTs in wires became denser with increasing irradiation dosage



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